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Osmotic theories, with special reference to van't Hoff's law

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Osmotic action is a phenomenon referred to in nearly all text-books on physics, in many works on physical chemistry, and in practically all books which deal with physiological phenomena, whether relating to plant or animal. In these same text-books, whether relating to physics, chemistry, or biology, one will look in vain for a satisfactory explanation of osmotic processes. In fact a variety of definitions will be found, some relating to diffusion merely, some relating to osmosis and diffusion in a general way, some relating to osmosis particularly, but all more or less vague; and, when relating to pressure produced by osmotic action, sometimes confusing and contradictory. Of course, osmotic activities in themselves are physical phenomena purely; but as they bear so important a part in relation to physiological operations, they are dealt with frequently in works on biology. But it is to the physical chemist, perhaps, to whom we must look for more light with respect to the operations underlying osmotic processes.

It is not intended here to go into a history of the subject, yet, in order to understand the question in its relationships, it is necessary to give a few points of a historical nature.

The phenomenon of osmosis, first observed in relation to organisms, crept into the text-books and other books on physics, and was dealt with there in connection with diffusion and dialysis rather than as osmosis merely. In such books we have to read through such terms as colloid and crystalloid before we come to osmosis. As a matter of fact, however, colloid and crystalloid

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have nothing to do with the subject, for* “The law of osmotic pressure holds for all substances no matter what the nature.” However, we have to know something of the meaning of these terms before we can interpret the statements and definitions given in the text-books on physics. The following statement† gives a common idea with regard to osmosis: “When liquids or gases force their way through porous septa and mix the diffusion is called osmose.” Now this would actually not be osmosis at all unless the septum is porous only to such an extent as will permit, yet hinder to some extent, the passage of the liquid. According to the definition given above, the process is diffusion merely. But since the term “force their way through,” is used, we have to conclude that it is not mere diffusion. The definition includes, therefore, something of a contradiction. In the following quotation is given another view of the osmotic action:‡ “In case of two liquids separated by a porous septum, the liquid which wets the septum the better, passes through the more rapidly.” This is intended to imply that the attraction which the septum has for the liquid is the factor including osmose, but this is not true in many cases, as for example in the case of the pig’s bladder and thistle-tube experiment. For example, when a little caustic potash has been added to the sugar solution which is placed on one side of the septum, and pure water on the other, the sugar solution, aided by the alkali, wets the membrane more quickly than pure water, yet the water passes through the membrane more readily, and the movement is inward. In fact, the sugar solution does not pass through at all, at least not for a considerable time. Referring to the subject of osmosis, Anthony & Brackett§ say “An explanation of these facts follows if we suppose that diffusion of a liquid through a continuous membrane can occur only when the liquid is capable of temporarily uniting with the membrane and forming part of it.” From this it appears that the membrane itself is the active agent in the process, and that osmotic pressure is due to the attraction and perhaps chemical action of the membrane.

Enough has been said about the general view of osmotic ac-

* Ostwald, *Outlines of general chemistry*, 128. 1895.

† Gage & Fessenden, *Text-book on physics*, 43. 1887.

‡ Appleton, *Chemical philosophy*, 132. 1897 [ed. 4].

§ *Text-book of physics*, 106. 1888 [ed. 4].

tion to show that we need more definite statements with regard to the subject. We need to remodel our ideas — if the quotations above can be taken as representative of them — because there is no subject more fundamental, more universal in plant and animal functions, than osmosis. And it is in this connection that we need something more definite than we have. The physiologist is confronted with osmotic phenomena at every turn, and he looks in vain for explanations which will satisfy the conditions he meets. Some theories meet with one condition, but not another.

We regard to osmotic pressure, it should be said that no definite measurements were made of it until Pfeffer* developed an apparatus based in its mechanism on the plant cell, but made of inorganic material, and capable of measuring the pressure set up by osmotic forces. Pfeffer's work was epoch-making in this respect, and practically all development made on osmotic measurements, both theoretical and experimental, has been based on Pfeffer's researches. The apparatus which Pfeffer prepared has been known as the "Pfeffer cell." This cell is composed of a porous earthenware cup like a battery jar, in the walls and bottom of which is a precipitate of copper ferrocyanide. This jar, when plugged and connected with a manometer, can be used to measure the pressure produced by osmotic action of certain given substances. This cell, though easily described, is extremely difficult to make, and in very few laboratories, so far as the writer can learn, has the Pfeffer cell been made to work successfully. Comparatively recently, however, the Pfeffer cell has been improved to a high degree by Morse and colleagues† at Johns Hopkins University, and used with great success on osmotic pressure investigations. The improvement to the Pfeffer cell has been mainly in the matter of extracting the air from the porous jar, and placing the membrane. This is done by means of an electric current which forces the liquid into the wall of the jar. The insertion of the stopper plug is a difficult operation also; in fact, where high pressures are to be recorded, the whole operation is one which requires the greatest care in every detail, and one which taxes the patience of the operator to the utmost. Morse and Frazer succeeded in preparing a

* *Osmotische Untersuchungen.* 1877.

† *Am. Chem. Jour.*, vols. 26, 28, 34, and others.

cell which sustained a pressure of 31 atmospheres, certainly an enormous pressure. Until the electrical method of arranging the cell was developed, a pressure of no such magnitude had ever been obtained.

Recently there has been prepared a good work on osmotic action and its bearing upon plants, by B. E. Livingston.* While this work covers the ground rather thoroughly, it does not refer to Morse's work, and it holds too strictly to van't Hoff's theory of osmotic pressure. However, Livingston's book is by far the most comprehensive and readable on the subject in the English language to-day.

With regard to the subject of osmotic *pressure*, four names stand out prominently, Pfeffer, Morse, van't Hoff, and de Vries — Pfeffer as the originator of the Pfeffer cell, Morse for the development of the cell for high pressure, van't Hoff for an expression of a theory of osmotic pressure, comparing the solute to a gas, and de Vries for recorded results of relative osmotic pressures in plants. It is mainly in regard to *osmotic pressure* and the theories advanced to explain it, that the present discussion is offered. The theory of van't Hoff is the one most generally accepted at the present time, and the only other one that has been offered is now considered rather old and insufficient. The chief objections to both theories are that they do not *explain*, and that, in several cases, they leave much to be desired in regard to several phases of osmotic phenomena. Van't Hoff's theory, when put into simple English, is as follows: "Dissolved substances exert the same pressure in the form of osmotic pressure as they would exert were they gasified, at the same temperature, without change of volume," and this idea has been widely accepted. The main reason for its general acceptance is that it seems to harmonize with certain other well-known physical laws; but van't Hoff himself does not appear to have had any experimental knowledge of the actual pressure which osmotic substances do exert. His law, as well as Ostwald's conclusions with regard to the magnitude of osmotic pressure, was based on Pfeffer's researches, and Pfeffer himself was not able to measure osmotic pressure when such pressure reached a point as high as five or six atmospheres. Pfeffer's work in this regard has

* Livingston, "The rôle of diffusion and osmotic pressure in plants." 1903.

been, in fact, the basis for all modern conceptions of osmotic pressure. His figures have entered into text after text, in both physics and chemistry. The work is now regarded as a classic, and van't Hoff's law gives it an emphasis which will carry it on through time, for many years yet. Now, van't Hoff's law does not explain the *cause* of osmotic pressure, it merely states it, and leaves the explanation to be inferred.

Let us point out some of the most serious objections to van't Hoff's law as it relates to osmotic pressure. It bases its argument, from the experimental side, on Pfeffer's researches and conclusions. These show several weaknesses which seriously affect van't Hoff's theory as well as Pfeffer's own figures. Pfeffer states that the osmotic pressure of cane sugar, when a gram molecular weight is dissolved in a liter volume, is 22.4 atmospheres and this is what it should be theoretically according to van't Hoff's theory. Sugar is not an electrolyte, hence no account is to be taken of dissociation. In looking into Pfeffer's work * to examine minutely the methods, this statement is found: "The same pressure (that is, 22.4 atmos.) must be exerted by a solution of 342 grams of cane sugar in 1 liter of water." Now, he surely could not have meant this as stated, because it is not in accord with some of his own statements, and is certainly not in accord with van't Hoff's law, or any ordinary interpretation of it. Moreover, further on is given, on pp. 146, 147 of Pfeffer's *Plant Physiology*, one statement referring to solution concentration; "1 gram in 100 c.cm. *of water*," and this refers to a column heading on the preceding page, "Osmotic pressure of 1 gram in 100 c.c. *of solution*." From this it appears as though he regarded the two statements, "dissolved in a liter of water," and "dissolved to a liter of solution" as the same thing. In the phrase "342 grams of cane sugar in one liter of water," we have a concentration quite different from that made by dissolving 342 grams to one liter of solution. The latter is that to which van't Hoff's theory directly applies. Theoretically, 342 grams to 1 liter volume gives 22.4 atmospheres pressure. Now, it may be said that Pfeffer made a mere typographical error, when he said "in 1 liter of water." Of course, neither Pfeffer, van't Hoff, nor Ostwald had ever actually developed a pressure of 22.4 atmospheres. Pfeffer used weaker solutions, and

* *Osmotische Untersuchungen*, 1877, and *Physiology of plants*, 1900.

from these he *calculated* what the pressure would be for stronger solutions. Supposing we assume that Pfeffer meant to say "342 grams in 1 liter solution" (and this is the only statement tenable if we are to harmonize it with van't Hoff's theory), we are led to an important conflict with Morse's actual experiment which shows that a solution containing 342 grams of cane sugar per liter (of solution), gives over 31 atmospheres pressure. We then arrive at this paradox—*theoretically*, the pressure should be 22.4 atmospheres; *actually*, it is over 31 atmospheres. This pressure of 31 atmospheres was actually obtained. In fact the pressure was more than this, but the apparatus (osmometer) burst at this enormous pressure, and the pressure may therefore be considered more. They conclude that a pressure of at least 32 atmospheres would result from a volume-normal-solution of cane sugar (342 grams per liter of solution).

The actual difference in volume between a solution made by dissolving 342 grams of cane sugar in one liter of solution, and that made by dissolving 342 grams of it in one liter of water is about 214.4 c.c. In the first case the volume is 1000 c.c. and in the latter the volume is 1214.4 c.c.

The following experiment shows also that the gas-pressure theory is not tenable. Pour a few c.c. of chloroform into a test-tube, then drop into this a crystal of iodine. The chloroform turns red from the dissolved iodine. Now pour very gently on top of this a few c.c. of water, and on top of the water a few c.c. of xylol to which has been previously added a crystal of iodine. The xylol dissolves the iodine and so we have one red liquid on top, and one on the bottom of the water. The water remains clear for days, weeks, and months, showing that none of the iodine passes from either the xylol or the chloroform to the water. According to the gas theory, it should do so. But if we carefully suspend by a wire, a crystal of potassic iodide in the water, then, after a short time, the iodine coloration is seen in the water. Some of the iodine has left one or other, or both neighboring liquids. The explanation of this is that the KI solution *attracts* the molecules of iodine from the other solutions. They are attracted *to* not forced *from*.* Morse gives the following expression which applies to

* Am. Chem. Jour. 34 : 91. 1905.

this: "The determining factor in osmotic pressure is the numerical ratio existing between the molecules of the dissolved substance and of the solvent, rather than the number of molecules of the dissolved substance which are contained in a unit volume of the solution." If we place in a tube the three liquids as above, but instead of pure water we substitute a water solution of iodine with potassic iodide, in a day or two the brownish solution in the center becomes colorless towards both top and bottom, while the chloroform and the xylol have turned reddish, showing that the iodine has passed into these liquids. Now if the dissolved iodine acted as a gas, we should have the water solution becoming lighter-colored, but uniformly so, and not light-colored at each end. When the iodine left the water to pass into the chloroform, other molecules of iodine would replace them from behind, if they were *driven* into the chloroform by "gas-pressure." Several other experiments with the liquids, also with turpentine, xylene, ether, and carbon disulphide have been made with colored substances in solution; and the conclusion reached from observation of these is that the pressure which we call osmotic pressure is due to *attraction*.

The Traube* pellicle affords a further illustration of the case in point. When the lump of CuCl_2 is dropped into the solution of potassium ferrocyanide a membrane is formed about the lump. Inside of this membrane is CuCl_2 solution, and outside is the ferrocyanide solution. The water is taken in through the membrane and into the CuCl_2 solution, thus increasing the volume. The membrane bursts and is immediately repaired. The process is continued with another rupture, and so on. Now, the point of rupture is always at, or near, the top of the sack of CuCl_2 solution. The solution of copper chloride is much more dilute at the top, yet, if the theory of "bombardment of molecules" were sound, it should rupture obviously where the molecules are most numerous, which is at the bottom. It can easily be seen that the solution is more dense at the bottom by the deep blue color, and it would naturally be so because of the very slow diffusion of the solute upwards. As has been said, the sack should rupture at the bottom, assuming the "gas-pressure" theory. The reason the sack ruptures at the top—an explanation not necessary, how-

* Described in Pfeffer, *Physiology of plants* 1: 106. 1900 [trans. by Ewart].

ever, to this discussion — is that the membrane is weaker at the top, owing to the fact that the copper chloride is less dense there, and the consequently less rapid chemical action ; and also to the fact that the membrane is not so old at, or near, the top. The phenomena which may be observed in the formation of the Traube pellicle present a strong argument against the “gas-pressure” theory.

Take a glass jar and place in it a bright, well-cleaned piece of zinc, or bright iron, then fill with distilled water, and cover tightly with a bladder parchment as for an osmometer. Now immerse the whole jar in a strong solution of copper sulphate. After a time the zinc (or iron) becomes coated over with a dark brown substance which proves to be copper, or copper oxide. If a similar experiment be made, but without the zinc strip, there is no copper sulphate found in the closed jar, even after a few hours. Now the only reasonable conclusion as to how the copper molecules, or ions, reached the zinc, is that they were *attracted* there by the zinc and not *driven* from behind.

The matter of interpretation, or explanation of the gas-theory as accounting for osmotic pressure, shows perhaps as forcibly as the experiment mentioned, that the theory of gas-pressure is wholly inadequate to the situation. Two or three illustrations of the conclusions reached by those basing their explanations on the “gas-pressure” theory may be given to demonstrate what such theory leads to. Take, for example, the explanation often given of osmotic pressure. Livingston* states it thus: “The following explanation of osmotic pressure has been given by various authors. The quotation is from Davenport [Experimental Morphology]: ‘Upon the side containing the greater number of molecules of salt [solute], fewer water [solvent] molecules will in a given time strike the membrane than upon the other side ; and since the number passing through is proportional to the number striking, relatively fewer molecules of water will consequently pass out, and so there will be a resultant flow of water to that side ; and if the mass of water is confined, it will exert great pressure.’ This explanation is untenable for several reasons. . . . Into this matter it is unnecessary to go farther than to add that osmotic pressure can be demonstrated as readily in solutions occupying less volume than the original solvent as in those occupying more. It is obvious

* The rôle of diffusion and osmotic pressure in plants.

that in the former case there must be a greater number of solvent particles per unit volume than in the pure solvent. Hence if the above explanation can be retained, there should be no osmotic pressure developed in such solution; indeed, it should appear on the side of the pure solvent."

Livingston gives in the book already named a more detailed argument than that quoted above to show the fallacy of the theory offered as explanation of osmotic pressure.

Now Livingston himself offers a theory which is objectionable perhaps to the same degree as that which he so thoroughly refutes. He says, p. 26, the pressure is "due to the bombardment of the walls by the solute particles," and, p. 31, "If there were available a membrane permeable to the solute but impermeable to the solvent, this diffusion tension of the solvent might be directly measured. It would be an osmotic pressure similar to that occasioned by the solute molecules, but of much greater magnitude and in the opposite direction." From this it appears as though both solute and solvent exerted osmotic pressure, and this is due to the "bombardment of the walls." But he says, p. 28, "Osmotic pressure is independent of the solvent and dependent only upon the number of particles of solute." Now the bombardment of the walls *outward* does not account for an *inflow* of water; in fact, it would, if anything, oppose the inflow. But he speaks of an osmotic pressure of the pure solvent. Now if this be so, the inflow would be due to this pressure and not to the bombardment of the walls in the opposite direction. He says, p. 30, "Water molecules pass . . . in both directions" and also "particles of solute hinder the escape of the solvent molecules." Yet, if the solute molecules were *bombarding outward*, there would be a greater tendency for a free course without hindrance for solvent molecules *outward*. From the above, the gist of the idea is that the pressure is due to the bombardment of the walls by the solute, and that water is forced in owing to the bombardment from within, because "The pressure produced by the solvent on one side of the membrane is practically equalled by that on the other side." Yet the crucial point is to account for the inflow of water, and it is not easy to see how water enters when there is no force exerted except a bombardment in the *opposite direction*.

One other illustration of a conclusion arrived at from the gas-pressure theory may be given. The statement has been made that if a solution strong osmotically were placed in a very thin glass flask (such as that used by physicists to demonstrate atmospheric pressure by exhausting the air and causing the flask to collapse), the flask would immediately explode because of the "bombardment of the molecules in solution." The experiment is the best proof of the fallacy of this notion. There is no osmotic pressure whatever in such a case and no explosion either. All these theories fall to the ground when examined closely. Now, it is not the intention here to show the insufficiency of these theories merely. The chief object in writing this discussion is to present a clear and reasonable theory, to explain *osmotic action* and particularly *osmotic pressure*; a theory is valuable only so long as it explains.

The theory proposed here postulates two things: (1) That a membrane can be less permeable to one liquid than to another. (2) That the molecules of all substances which are soluble in a certain solvent have an attraction for the molecules of the solvent and the molecules of the solvent for the substance in solution. In regard to the former of these two postulates, it may be said it is entirely comprehensible that a membrane may permit one body to pass through a pore more readily than another, because of the relative size or shape of pore and molecule, and because of friction offered by the membrane to the passage of the molecule. The second postulate above mentioned refers to a condition so common in nature that it scarcely needs a word of comment. All molecules are probably endowed by nature with this attractive force, but it must not be forgotten that this force operates only at very minute distances. To be more explicit, let us take an example. Choosing the common osmometer having a sugar solution within and water without the pig's bladder membrane; suppose the sugar molecule to be too large to pass through the pores of the bladder, and that these pores are large enough to permit the water molecules to pass with little or no opposition, the molecules of sugar attract the molecules of water and both tend to move toward each other. The sugar molecules are prevented from moving through the membrane, but the water is not, hence there is an *inflow* of water, due to attraction. This attraction, then, is the *force* which

underlies osmotic pressure. The operation tends to show that osmotic pressure is, however, regulated by the character of the membrane, and this character depends upon two things; the size of the pores, and the actual relative attraction which the membrane has for the solvent and for the substance in solution. Osmotic processes are not different from diffusion. The membrane simply *shows this diffusion*.

Now, the actual amount of pressure developed by a substance in solution will obviously depend upon the number of molecules (or ions) in a given volume of the solution, hence any other conditions, such as freezing point or boiling point, which have to do with molecular activities, will not likely be very different from osmotic phenomena. And in this connection, it is easy to realize that such attraction as that postulated for osmotic pressure might very probably be different in one substance from that in another. From this it is easy to account for the high pressure of potassium nitrate as compared with sugar, in equimolecular solutions, *without assuming the dissociation theory*. In this case, there is no necessity for assuming ionization. The cause of the high pressure in one case as compared with that in another, is due to the specific attraction of the molecule of the potassium nitrate, and not to the assumption that there are two bodies or ions of K and NO_3 , instead of one KNO_3 body. If we assume the dissociation theory to account for the relatively high pressure of such substances as are called electrolytes, we must ascribe as much attractive force to each ion as to the whole molecule, which is a more unreasonable assumption than to ascribe to one molecule of a different kind a greater attractive force than to that of another. In the former case, we have to say, not that "The whole is greater than its part," but that each part is equal to the whole, which, if not unreasonable, is hovering near it. Jost* alludes to "each free ion having the same osmotic value as the entire molecule." To prove this incorrect, is, of course, not easy, but the burden of proof must rest on those who advance that theory. The dissociation theory itself is without much support, and in physiological problems it gives no light. There are so many physiological operations at variance with it that we need not assume the theory

* Plant physiology, 16. 1907 [Eng. trans.].

of ionization at all. In fact, Jost admits this in the following quotation: "However, botanical investigations on the amount of osmotic pressure are entirely independent of this physical theory." The absorption of soil water by plants is a function which cannot be explained on the gas-pressure theory, but is capable of reasonable explanation on the theory of attraction.

With regard to solutions of two or more substances, the statement is generally made that osmotic pressure is the sum of the individual pressures; quoting from Livingston, p. 29, "The total osmotic pressure of a dilute solution of mixed solutes is the sum of the partial osmotic pressures of the component solutes." But, in some cases, this is not true. If we measure the osmotic pressure of a dilute NaCl solution, and then add some CaCl_2 to this solution, there is no increase in osmotic pressure. This has been borne out by Osterhout* in his experiments on plasmolysis which he performed upon certain algae. He applied a NaCl solution to the alga, and brought about plasmolysis. He then added some CaCl_2 to a similar solution of NaCl and applied this mixed solution to a similar alga. In this case, the plasmolysis did not occur, although the solution was stronger osmotically. In the matter of determining the osmotic pressure of mixed solutions, very little has so far been done. What has been done, however, seems to show that no one can predict *a priori* just what the sum total pressure of mixed solutions will be. As far as plasmolytic operations have been used to demonstrate relative osmotic pressure, it may be inferred that the specific characters of the substances in solution are the determining factors; and that these may differ with different plants. If, however, we assume the theory proposed here—that of specific attraction—these phenomena are easily explained. In mixed solutions, the various molecules of solutes quite probably exert an attraction upon one another, as well as upon the solvent; and, to some extent at least, it may be supposed that whatever attraction a substance might have when alone in solution, would be modified by the presence of molecules of other solutes. Hence, it is not difficult to account for the modified osmotic pressure of such mixed solutions.

In plant and animal functions, it is mixed solutions mainly

* Bot. Gaz. 46: 54. 1908.

with which we are concerned. The "gas-pressure" theory affords no explanation, while the theory of attraction gives a foundation for reasonable explanations of all such phenomena. Root absorption, as a function of plants, is one which, as far as the text-books are concerned, is explained by the statement that the force causing absorption is osmotic pressure. To apply van't Hoff's "gas-pressure" theory with a view to an explanation of the process is next to impossible, for the osmotic pressure is *within* the cell of the plant, and it is not easy to see how such pressure acting *outward* could cause an *inflow* of water. It should also be considered that we have to account for, not only the inflow of water, but also the inflow of substances in solution. The theory of attraction is quite applicable to these activities, and it furnishes a reasonable explanation from the fact that a disturbance of the content of soil water, by the addition of another solute, may render what the soil contained previously to this addition more (or less) available to the plant; because in the theory here advanced, it is assumed that solutes have an attraction for one another as well as for the solvent. When a solution is saturated, this attraction is practically satisfied; or more explicitly, it is counteracted by the attraction of one molecule for another of its kind in the process of crystallization.

With regard to the relatively high osmotic pressure said to be produced in plant cells, it may be said that the method is founded entirely upon van't Hoff's theory and Pfeffer's calculations; and as employed to estimate such pressure, it is open to serious objection. The method of finding the osmotic pressure in a given cell is to use a solution of known osmotic strength (?), and if this *just* induces plasmolysis, the cell sap of the plant is said to be of equal osmotic pressure. But it has been shown by Osterhout, previously cited, that distilled water may, under certain conditions, bring about plasmolysis; also that the addition of CaCl_2 to a solution of NaCl which has produced plasmolysis, will actually restore turgor, although the external solution is now stronger osmotically. Moreover, it is not yet known experimentally just what is the magnitude of the osmotic pressure of most of the solutions which have been used in plasmolysis, hence the conclusions are open to objection.

A word about ionization. The attraction theory does not assume ionization, though not inconsistent with it. Physiological investigation gives no support to the theory of dissociation, and osmotic pressure need not assume it. The strongest argument in favor of dissociation is the electrical conductivity, but the very current brought to bear upon the solution may actually *induce* the condition which, by the ionization theory it is assumed exists there *before* the electrodes are applied. It is not intended here to go into any discussion of the theory of dissociation further than to state that osmosis, or osmotic pressure, does not furnish any data for such theory. Osmosis and osmotic action can be explained fully without the assumption of dissociation or ionization. And these statements are made with full knowledge of the fact that the relatively high pressure of such substances as KNO_3 was taken as one basis for the assumption of dissociation.

The theory of surface tension to account for osmotic pressure has been advanced, but, from the physiological side, it can receive no support. Surface tension is something which depends upon the attraction of the molecules of the solvent for one another, and that only in the most minute distances; and is developed only in a few layers of molecules on the extreme surface. It cannot account for osmotic pressure or other osmotic phenomena.

More recently other theories, more or less directly connected with the attraction theory, have been advanced in opposition to van't Hoff's gas-pressure theory.

Perhaps the most important of these is the discussion offered by Kahlenberg* in which he opposes vigorously the gas-pressure theory. So far, we agree with him thoroughly, but the main point of difference between Kahlenberg's argument and that offered in this discussion lies in the fact that Kahlenberg ascribes to the membrane a large portion of that factor which the attraction theory ascribes to the molecules of solute and solvent.

Some of his experiments, notably that employing the three substances — chloroform, water, and ether — and which he calls a "typical case of osmosis," can scarcely be considered osmosis at all, for it is only a mixing of three liquids possessing varying degrees of solubility for one another. Water in this case would

* Trans. Wisconsin Acad. 15: 209. 1904.

be called the membrane. We cannot follow him so far as this, for in speaking of the membrane, he says, "The substance must be soluble in the membrane." In some of his experiments the membrane was dissolved to some extent by the liquid in contact, but so far as it was soluble, the condition was not "typical osmosis." Solubility of the membrane is not necessary. For instance, if we use parchment paper (butter paper) and two liquids, (1) water, (2) sugar solution, these arranged for an osmometer will give about one third of an atmosphere pressure without extra support. There is no solubility whatever of the membrane in either liquid.

On the other hand, we agree with Kahlenberg in the following (*loc. cit.* 271): "To speak of osmotic pressure of any isolated solution . . . is nonsense." . . . And further, to assume that solutes are polymerized or dissociated in dilute solutions because the osmotic pressures developed by the latter in given cases happen to deviate from values computed from the gas laws is evidently equally unjustifiable practice." We do not differ materially from him with respect to the moving force causing osmotic pressure, excepting in the name he employs; namely, chemical affinity. We think this term not happily chosen because the affinity is purely a *physical* one, and not chemical. There is no chemical change whatever. If there be chemical action involved in the operation thus far, it is not osmosis. From the above statement, it must not be assumed that we undervalue the influence of the membrane as a part of the operation. The membrane is absolutely essential. It is a *sine qua non*, but it is merely a screen between the two liquids.

The gas-pressure theory has also been attacked from another point of view, quoting from *Nature* 72: 541: "Batelli and Stefanini have brought forward, however, a number of facts which, if subsequently verified, are likely to prove insuperable objections to its [the van't Hoff law's] validity. . . . It is contended that osmotic pressure is essentially a capillary phenomenon." To what extent this may hold good will depend upon how far the idea of capillarity is carried, and if it is used in its broadest sense, the capillary idea is not far removed from that offered in this discussion—that of *attraction*.

A summary of the salient points of this discussion, and of the experiments involved, presents the following: The chief argu-

ments against the gas-pressure theory are : (1) Morse's experiments with sugar solutions show an osmotic pressure of about 32 atmospheres in a gram-molecular weight per liter solution, when it should, by van't Hoff's law, be only 22.4 or thereabouts. (2) The writer's own experiments with colored solutions of various kinds and with different solvents, also his physiological experiments concerned with absorption and with cell sap. (3) Osterhout's experiments on plasmolysis. (4) Many operations connected with living plants, *e. g.*, the formation of ice (in freezing weather) in the intercellular spaces, the formation of calcium oxalate crystals outside the living cells, and others. (5) The growth of the Traube pellicle. (6) Kahlenberg's experiments and discussions.

The Attraction Theory here proposed is not only in harmony with all the phenomena presented as argument against the gas-pressure theory, but it affords a reasonable explanation in each and every case. This theory is not claimed to be entirely new, for it was used, in part here and there, many years ago, but was never applied generally enough, hence it was not surprising to find van't Hoff's law superseding. But van't Hoff's law shows so many weak points that it cannot be accepted as explanatory of osmotic pressure.

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